

# METHOD OF CLEANING A SUBSTRATE

## CROSS REFERENCE TO RELATED APPLICATION

This application claims priority under 35 USC § 119 to Korean Patent Application  
5 2003-11785, filed on February 25, 2003, the contents of which are herein incorporated  
by reference in their entirety for all purposes.

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

10 The present invention relates to a method of cleaning a substrate, and more  
particularly to a method of cleaning a substrate that includes a metal thin film pattern  
formed thereon.

### 2. Description of the Related Art

Recently, as information processing systems have been widely utilized,  
15 semiconductor devices have been rapidly developed. The semiconductor devices are  
required to have improved performance characteristics such as high response speed as  
well as large storage capacity. To meet these requirements, semiconductor  
manufacturing technology has been developed so that the semiconductor devices have  
high response speed, enhanced reliability, high integration density, etc.

20 As semiconductor manufacturing technology is rapidly developed, contaminants  
such as particles or polymers are precisely controlled in semiconductor manufacturing  
processes. Though the contaminants are accurately controlled, various contaminants  
are frequently attached on the surface of a semiconductor substrate during the  
semiconductor manufacturing process. Hence, cleaning processes are commonly

performed on the semiconductor substrate to remove the contaminants from the substrate. The cleaning processes for the semiconductor substrate are generally divided into two types, namely, a wet cleaning process using a cleaning solution and a dry cleaning process using a gas.

5       As for the wet cleaning process, a semiconductor substrate is immersed in a cleaning solution including deionized water and/or a reactive solution after the cleaning solution is deposited in a bath. Alternatively, the cleaning solution is sprayed onto the semiconductor substrate to remove the contaminants from the semiconductor substrate. The cleaning solution typically includes a hydrochloric acid solution, an aqueous  
10 ammonia solution or hydrogen peroxide solution in addition to the deionized water.

There is disclosed a method of cleaning a semiconductor substrate using a cleaning solution including a hydrochloric acid solution, an aqueous ammonia solution and hydrogen peroxide solution in Japanese Laid-Open Patent Publication No. 1985-7233 and Korean Laid-Open Patent Publication No. 2001-56346.

15       Additionally, in the wet cleaning process, a magnetic agitator or mega-sonic energy may be employed to improve the efficiency of the cleaning process.

When a semiconductor substrate is cleaned by a wet cleaning process utilizing the mega-sonic energy, the semiconductor substrate is cleaned in a bath coupled to a mega-sonic energy generating member. When the mega-sonic energy is applied to the  
20 semiconductor substrate immersed in a cleaning solution in the bath, the efficiency of the cleaning process may be improved. The mega-sonic energy bursts the gas bubbles included in the cleaning solution to accelerate the cleaning process for the semiconductor substrate. That is, the gas bubbles formed in the cleaning solution are ruptured by the mega-sonic energy to generate burst pressure and temperature variation

of the cleaning solution, thereby removing the contaminants attached to the semiconductor substrate.

There are disclosed methods of cleaning a substrate also utilizing the mega-sonic energy in Korean Patent No. 242,271 and Japanese Patent Laid-Open Publication No. 1990-257632. When the substrate is cleaned by such methods using a cleaning solution and the mega-sonic energy, the contaminants on the substrate may be effectively removed. However, the substrate may be impaired due to the mega-sonic energy applied during cleaning the substrate. In particular, when a metal pattern is formed on the substrate, the metal pattern may be seriously corroded during cleaning the substrate by employing those methods.

Additionally, in the method of cleaning a semiconductor substrate utilizing the mega-sonic energy, failure of a metal pattern may occur when the mega-sonic energy applied to the semiconductor substrate is relatively high. That is, when high mega-sonic energy is applied to the substrate that includes the metal pattern, the metal pattern may be broken during cleaning of the semiconductor substrate.

Therefore, there is required a method of cleaning a substrate which reduces the corrosion of the metal patterns formed on the substrate and minimizes the damage of the substrate or the metal pattern.

## SUMMARY OF THE INVENTION

In order to overcome above-mentioned problems, a feature of the present invention is to provide a method of effectively cleaning a substrate without causing damage to the substrate and the metal wiring formed on the substrate.

In accordance with one aspect of the present invention, an aqueous sulfuric acid

solution diluted by deionized water is applied onto a substrate. Contaminants on the substrate are cleaned in accordance with the reaction between the diluted aqueous sulfuric acid solution and the contaminants by applying a mega-sonic energy to the substrate including the diluted aqueous sulfuric acid solution.

5        The mega-sonic energy can be generated using a power of about 5 Watts to about 15 Watts. The diluted aqueous sulfuric acid solution includes the deionized water and sulfuric acid by a volume ratio of about 500: 1 to about 8,000: 1, and the sulfuric acid has a concentration of about 10 ppm to about 1,000 ppm. The substrate is cleaned at a temperature of about 20 degrees C to about 30 degrees C for about 30 seconds to  
10    about 120 seconds.

The substrate being cleaned may have structures such as a metal wiring or a metal thin film formed thereon. The aqueous sulfuric acid solution may be applied while the substrate is rotated at a speed of about 8 rpm to about 50 rpm.

In one embodiment, cleaning the substrate is performed using a spin scrubber.  
15    The substrate can be provided in the spin scrubber in a batch type. The diluted aqueous sulfuric acid solution can be applied by a spray process, and the mega-sonic energy can be applied through a bar facing the substrate. In one embodiment, the substrate is rinsed using deionized water and dried.

In accordance with another aspect of the present invention, after an aqueous  
20    sulfuric acid solution diluted by deionized water is provided in a bath, the substrate, which can have a metal wiring or a metal thin film formed thereon, is immersed into the diluted aqueous sulfuric acid solution. The contaminants on the substrate are removed in accordance with the reaction between the diluted aqueous sulfuric acid solution and the contaminants by applying mega-sonic energy to the substrate including the diluted

aqueous sulfuric acid solution.

According to the present invention, the contaminants on a substrate can be effectively removed and the metal wiring formed on the substrate is not corroded when a cleaning solution includes a diluted aqueous sulfuric acid solution and mega-sonic energy is applied to the substrate during a cleaning process. Thus, a reliability of a semiconductor device may be improved and the throughput of a semiconductor manufacturing process may be enhanced. Additionally, appropriate mega-sonic energy is applied to the substrate in the cleaning process so that the failure of the metal wiring such as a short may be prevented.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the invention will be apparent from the more particular description of a preferred embodiment of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

FIG. 1 is a schematic cross-sectional view illustrating a spin scrubber employed for performing a method of cleaning a substrate according to one embodiment of the invention.

FIG. 2 is a schematic cross-sectional view illustrating a bath employed for performing a method of cleaning a substrate according to another embodiment of the invention.

FIG. 3 is a flow chart illustrating the method of cleaning a substrate according to one embodiment of the invention.

FIG. 4 is a flow chart illustrating the method of cleaning a substrate according to another embodiment of the invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

5       The cleaning solution that can be used in the present invention includes an aqueous sulfuric acid solution diluted by deionized water. When sulfuric acid diluted in the diluted aqueous sulfuric acid solution has a concentration of below about 10 ppm, the efficiency of a cleaning process that is performed on the substrate using the diluted aqueous sulfuric acid solution may be reduced. Also, the substrate, especially the metal  
10       wiring formed on the substrate, may be damaged during the cleaning process using the diluted aqueous sulfuric acid solution when the sulfuric acid diluted in the diluted aqueous sulfuric acid solution has a concentration of above about 1,000 ppm. Therefore, the sulfuric acid diluted in the diluted aqueous sulfuric acid solution preferably has a concentration of about 10 ppm to about 1,000 ppm.

15       When the volume ratio between the deionized water and the sulfuric acid is below about 500: 1, the substrate may be impaired during the cleaning process. However, when the volume ratio between the deionized water and the sulfuric acid is above about 8,000: 1, the efficiency of the cleaning process for the substrate may be reduced. Accordingly, in the present invention, in the diluted aqueous sulfuric acid solution, the  
20       volume ratio between the deionized water and the sulfuric acid is preferably about 500: 1 to about 8,000:1.

When the diluted aqueous sulfuric acid solution is applied as a cleaning solution to a substrate including a metal wiring or metal thin film, the corrosion of the metal wiring may be effectively prevented. Thus, the cleaning solution including diluted

aqueous sulfuric acid solution is advantageously employed for the substrate having the metal wiring or the metal thin film formed thereon.

The cleaning solution can be provided onto the substrate using one of at least two processes such as a spray process and an immersion process.

5        FIG. 1 is a schematic cross-sectional view illustrating a spin scrubber employed for performing a method of cleaning a substrate according to one embodiment of the present invention.

10        To clean a substrate 10 using the spray process, a cleaning apparatus includes a spin scrubber as shown in FIG. 1. The spin scrubber is a batch type including a chuck 12 and a nozzle 14.

The substrate 10 including the metal wiring is loaded on the chuck 12, and the cleaning solution is provided onto the substrate 10 from the nozzle 14. That is, the cleaning solution is applied onto the substrate 10 by a spray process using the nozzle 14.

15        When the cleaning process is performed on the substrate 10, the cleaning solution is sprayed onto the substrate 10 through the nozzle 14 while the substrate 10 is rotated in accordance with the rotation of the chuck 12. When the rotation speed of the substrate 10 is below about 8 rpm, the cleaning solution may not be uniformly sprayed onto the substrate 10 from the nozzle 14. That is, the cleaning solution may not reach to  
20        the peripheral portion of the substrate 10 because the centrifugal force caused by the rotation of the substrate 10 is relatively weak. When the rotation speed of the substrate 10 is above about 50 rpm, the cleaning solution may be rapidly splashed from the surface of the substrate 10. That is, since the centrifugal force caused by the rotation of the substrate 10 is too high, the cleaning solution may splash from the substrate 10.

Thus, the rotation speed of the substrate 10 is preferably about 8 rpm to about 50 rpm.

In addition, a mega-sonic energy generating construction is provided in order to apply mega-sonic energy to the substrate 10 where the cleaning solution is sprayed during the cleaning process. For this reason, the spin scrubber further includes a  
5 mega-sonic energy transmitting member 16 that applies the mega-sonic energy to the substrate 10 including the cleaning solution sprayed thereon.

The mega-sonic energy transmitting member 16 includes a power generating section 16b and a bar 16a extended toward the substrate 10 from the power generating section 16b. The power generating section 16b generates the mega-sonic energy and  
10 the bar 16a applies the mega-sonic energy to the cleaning solution sprayed on the substrate 10. The bar 16a faces the surface of the substrate 10.

When the mega-sonic energy applied to cleaning solution sprayed on the substrate 10 is weak, the efficiency of the cleaning process may not be effective. However, when the mega-sonic energy applied to the cleaning solution from the  
15 mega-sonic transmitting member 16 is too high, the substrate 10 may be damaged during the cleaning process. Hence, the mega-sonic energy transmitting member 16 applies appropriate mega-sonic energy to the substrate 10 including the cleaning solution sprayed thereon. The amount of the mega-sonic energy is can be substantially determined in accordance with the power generated from the power generating section  
20 16b. Preferably, the power generating section 16b generates a power of about 5 Watts to about 15 Watts in order to apply the appropriate mega-sonic energy to the substrate 10. The cleaning process is preferably performed at a temperature of about 20 degrees C to about 30 degrees C for about 30 seconds to about 120 seconds.

The cleaning mechanism using the cleaning solution and the mega-sonic energy

will be described.

When the cleaning solution is sprayed on the substrate 10, the cleaning solution is applied as a thin film having a predetermined thickness in accordance with the rotation of the substrate 10. Then, the mega-sonic energy is applied to the cleaning solution sprayed on the substrate 10. As the diluted aqueous sulfuric acid solution of the cleaning solution is chemically reacted with the contaminants formed on the substrate 10, the contaminants such as polymers or particles are removed from the substrate 10 according to the chemical reaction between the diluted aqueous sulfuric acid solution and the contaminants. Additionally, the gas bubbles included in the cleaning solution are burst by applying the mega-sonic energy to the cleaning solution. The rupture of the gas bubbles in the cleaning solution provides bursting pressure and changes the temperature of the cleaning solution, thereby facilitating the physical reaction between the cleaning solution and the contaminants. As a result, any contaminants existing on the substrate 10 are more effectively removed from the substrate 10.

After the contaminants on the substrate 10 are removed from the substrate 10 by using the scrubber and the cleaning solution, the substrate 10 is rinsed using deionized water. Then, the rinsed substrate 10 is dried to remove the moisture or water drops on the substrate 10. Here, the moisture or water drops on the substrate 10 are removed by a dry process using a nitrogen gas or by a wet process using isopropyl alcohol.

As described above, the efficiency of the cleaning process performed using the spin scrubber can be improved by spraying the cleaning solution on the substrate and by applying the mega-sonic energy to the cleaning solution. Particularly, since the cleaning solution includes the diluted aqueous sulfuric acid solution, the efficiency of the cleaning solution can be more improved. Further, the damage of the substrate can be reduced

during the cleaning process because the appropriate mega-sonic energy is advantageously applied to the substrate 10.

The immersion process for cleaning the substrate will be described.

FIG. 2 is a schematic cross-sectional view illustrating a bath employed for performing a method of cleaning a substrate according to another embodiment of the invention

Referring to FIG. 2, a cleaning apparatus includes a bath 22 to perform the immersion process for cleaning a substrate 20 including a metal wiring or metal thin film formed thereon. A cleaning solution is received in the bath 22, and the substrate 20 is immersed into the cleaning solution.

As described above, a mega-sonic energy transmitting member 26 is connected to the bath 22 to apply mega-sonic energy to the substrate 20 immersed in the cleaning solution. The mega-sonic energy transmitting member 26 includes a power generating section 26b and a bar 26a. The power generating section 26b generates the mega-sonic energy, and the bar 26a applies the mega-sonic energy to the substrate 20 immersed in the cleaning solution. Here, the bar 26a of the mega-sonic energy transmitting member 26 is positioned at the lower portion of the bath 22 under the substrate 20 having the metal wiring. The mega-sonic energy generated from the power generating section 26b is applied to the substrate 20 through the bar 26a. As described above, appropriate mega-sonic energy may be applied to the substrate 20. Thus, the power generating section 26b has a power of about 5 Watts to about 15 Watts to generate the appropriate mega-sonic energy. Preferably, the cleaning process is performed on the substrate 20 having the metal wiring at a temperature of about 20 degrees C to about 30 degrees C for about 30 seconds to about 120 seconds.

After contaminants on the substrate 20 are removed from the substrate 20 using the cleaning solution received in the bath 22, the substrate 20 is rinsed and dried as described above.

FIG. 3 is a flow chart illustrating a method of cleaning a substrate according to one embodiment of the invention.

Referring to FIGS. 1 and 3, in step S31, the substrate 10 including a metal wiring or a thin metal film is loaded on the chuck 12. The substrate 10 is rotated by predetermined rotation speed using the chuck 12 in step S33. In step S35, a cleaning solution including a diluted aqueous sulfuric acid solution is sprayed onto the rotating substrate 10 having the metal wiring. Here, the cleaning solution is provided around the central portion of the substrate 10. Because the substrate 10 rotates during spraying of the cleaning solution, the cleaning solution is uniformly dispersed from the central portion of the substrate 10 to the peripheral portion of the substrate 10. Thus, the cleaning solution is sprayed on the substrate 10 as a film. Contaminants, for example, particles or polymers, existing on the substrate 10 are primarily removed by spraying the cleaning solution. That is, the contaminants are removed from the substrate 10 in accordance with the chemical reaction between the cleaning solution and the contaminants.

Then, a mega-sonic energy transmitting member 16 applies mega-sonic energy to the substrate 10 where the cleaning solution is sprayed. The gas bubbles included in the cleaning solution are burst by the mega-sonic energy to provide bursting pressure and the variation of a temperature. Hence, the contaminants on the substrate 10 are secondarily removed from the substrate 10 by the bursting pressure and the variation of the temperature caused by the rupture of the gas bubbles.

After the substrate 10 is rinsed in step S39, the rinsed substrate 10 is dried in step S41.

FIG. 4 is a flow chart illustrating the method of cleaning a substrate according to another embodiment of the present invention.

5 Referring to FIGS. 2 and 4, a cleaning solution including a diluted aqueous sulfuric acid solution is received in the bath 22 in step S51. In step S53, the substrate 20 having a metal wiring or a metal thin film is immersed into the cleaning solution received in the bath 22. In addition, mega-sonic energy is applied to the substrate 20 from a mega-sonic energy generating member 26. Thus, contaminants existing on the substrate  
10 20 are removed by the cleaning solution and the mega-sonic energy. In this case, the contaminants on the substrate 20 are chemically removed by the cleaning solution, and also physically removed by bursting pressure and the temperature variation of the cleaning solution. The bursting pressure and the temperature variation of the cleaning solution are generated from the rupture of the gas bubbles included in the cleaning  
15 solution.

The substrate 20 is rinsed in step S55, and then is dried in step S57.

As described above, the efficiency of the cleaning process can be improved because of the cleaning solution including the diluted aqueous sulfuric acid solution and the mega-sonic energy. Additionally, since the appropriate mega-sonic energy is applied  
20 to the substrate, the substrate may not be damaged during cleaning the substrate.

Hereinafter, an example and comparative examples of the invention will be described.

#### Example

A diluted aqueous sulfuric acid solution was prepared as a cleaning solution for a substrate having a metal thin film formed thereon. Here, the volume ratio between sulfuric acid and deionized water in the diluted aqueous sulfuric acid solution was about 1: 1,000. The substrate was cleaned with the diluted aqueous sulfuric acid solution using a spin scrubber. The cleaning process was performed on the substrate at a temperature of about 30 degrees C for about 30 seconds. The substrate was rotated by a rotation speed of about 30 rpm during the cleaning process. Additionally, mega-sonic energy generated using a power of about 14 Watts was applied to the substrate on which the diluted aqueous sulfuric acid solution was sprayed. As a result, the contaminants existing on the substrate were removed by about 60 percent without corrosion of the metal thin film formed on the substrate.

#### Comparative Example 1

A substrate was cleaned according to the above-described process except for the type of cleaning solution. In this case, the cleaning solution included deionized water only.

Though the metal thin film formed on the substrate was not corroded, the contaminants on the substrate were minutely removed by about 2 percent.

#### Comparative Example 2

A substrate was cleaned according to the above-described process except a cleaning solution including hot deionized water only.

The metal thin film formed on the substrate was seriously corroded as well as the contaminants existing on the substrate were slightly removed by about 10 percent.

### Comparative Example 3

A substrate was cleaned according to the above-described process except for the type of cleaning solution. The cleaning solution included an aqueous ammonia solution and deionized water by a volume ratio of about 1: 1,000.

The metal thin film formed on the substrate was seriously corroded although the contaminants existing on the substrate were removed by about 68 percent.

As a result, when the substrate is cleaned using the cleaning solution including the diluted aqueous sulfuric acid solution, the contaminants on the substrate are effectively removed from the substrate while the metal thin film on the substrate is not corroded.

As described above, the contaminants on a substrate can be effectively removed and the metal wiring formed on the substrate is not corroded when a cleaning solution includes a diluted aqueous sulfuric acid solution and mega-sonic energy is applied to the substrate during a cleaning process. Thus, a reliability of a semiconductor device may be improved and the throughput of a semiconductor manufacturing process may be enhanced.

Additionally, appropriate mega-sonic energy is applied to the substrate in the cleaning process so that the failure of the metal wiring such as a short may be prevented. While this invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.